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Rotationally resolved $A^2\Pi_u \leftarrow X^2\Pi_g$ electronic transition of NC_6N^+

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The rotationally resolved $A^2\Pi_u \leftarrow X^2\Pi_g$ electronic origin band spectrum of dicyanodiacetylene cation, NC_6N^+ , has been recorded in the gas phase using frequency-production double modulation spectroscopy in a liquid nitrogen cooled hollow cathode discharge and cavity ring down spectroscopy in a supersonic plasma. The analysis of the complementary results provides accurate molecular parameters for the two spin-orbit components in both electronic states. © 2002 American Institute of Physics. [DOI: 10.1063/1.1427710]

I. INTRODUCTION

In recent years several cyanopolyacetylene radicals (HC_nN) have been studied by Fourier transform microwave spectroscopy^{1,2} and, following their laboratory detection, species as large as HC_{11}N have been identified by radio astronomy in the interstellar medium.³ The dicyano derivatives (NC_nN) may be comparably abundant in space, but are unsuitable for microwave detection due to absence of a dipole moment. In this case accurate spectroscopic information can be obtained from high resolution studies of vibrational or electronic transitions in the gas phase. The latter are available for a series of carbon chain radicals. Examples are the nonpolar NC_5N (Ref. 4) and HC_7H ,^{5,6} as well as chains that were already detected in dense interstellar clouds such as HC_6N (Ref. 6) and C_6H .⁷ These species are formed in ion-molecule reactions and consequently spectroscopic information on carbon chain ions is needed as well, but high resolution data are rare and pure rotational spectra are limited to a few species.⁸

This is particularly true for the (di)cyanopolyacetylene cations. Electronic spectra have been recorded in neon matrices for NC_{2n}N^+ ($n=2-6$) and $\text{HC}_{2n+1}\text{N}^+$ ($n=2-6$).⁹⁻¹² Following these and low resolution emission studies¹³⁻¹⁵ the rotationally resolved electronic gas phase spectrum of the cyanodiacetylene (HC_5N^+) and dicyanoacetylene (NC_4N^+)¹⁶ as well as the cyanotriacetylene (HC_7N^+)¹⁷ were reported. In the present work the rotationally resolved spectrum of the next larger member in the dicyano-series, NC_6N^+ , is presented. The results are compared with the results of density functional theory calculations¹⁸ and the spectroscopic parameters available for the iso-electronic chains HC_7N^+ (Ref. 17) and HC_8H^+ .¹⁹

II. EXPERIMENT

The spectra are recorded using two complementary experimental approaches. These are frequency production double modulation (FPM) spectroscopy of a static plasma generated in a discharge cell ($T_{\text{rot}} \sim 150$ K) and cavity ring-down (CRD) spectroscopy sampling a supersonic planar

plasma ($T_{\text{rot}} = 15$ K), yielding spectra with significantly different rotational profiles. Both experimental techniques have been described. In the FPM experiment²⁰ mixtures of 0.5%–0.6% cyanogen/He are discharged in a liquid nitrogen cooled hollow cathode incorporated into a White-type multiple reflection cell ($L_{\text{tot}} \sim 100$ m). Production modulation is obtained by applying a rectified 17 kHz ac voltage (–500 to 700 V). The laser beam is electro-optically modulated at a radio frequency of 192 MHz and detected by a fast photodiode. Subsequent phase sensitive demodulation of the high frequency portion of the signal during a production cycle gives absorption bands that have a derivativelike shape. The resolution is Doppler limited and typically of the order of 550 MHz.

In the CRD setup²¹ the NC_6N^+ radicals are formed by a discharge through a high pressure gas pulse (typically 100 mA at –1000 V for a 12 bar backing pressure) of an 0.2% cyanogen/He mixture in the throat of a $3\text{ cm} \times 300\text{ }\mu\text{m}$ multilayer slit nozzle device. A standard CRD spectrometer is used to detect the signals in direct absorption. The resolution is limited by the bandwidth of the laser to $\sim 0.035\text{ cm}^{-1}$. In both experiments iodine spectra are used for an absolute frequency calibration.

III. RESULTS AND DISCUSSION

An overview scan of the $A^2\Pi_u \leftarrow X^2\Pi_g$ electronic origin band transition of NC_6N^+ recorded by FPM in the discharge cell is shown in Fig. 1. In the range $15\,240\text{--}15\,248\text{ cm}^{-1}$ approximately 200 individual absorption lines are resolved. These transitions belong to the *P*-, *Q*- and *R*-branches of two subbands corresponding to the parallel $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ and $A^2\Pi_{1/2} \leftarrow X^2\Pi_{1/2}$ electronic transitions. The intensity ratio of the two bands is determined by the “spin-orbit temperature” and the value of the spin-orbit splitting (A'') in the ground state. The latter is estimated from previous studies to be of the order of $-40(5)\text{ cm}^{-1}$,¹⁶ the minus indicating that the $\Omega = \frac{3}{2}$ spin-orbit component is lower in energy than the $\Omega = \frac{1}{2}$. At the high ambient temperature in the cell both spin-orbit components are equally intense. The rotational population is distributed over many levels and the intensity of both *Q*-branches and transitions starting from low *J*-levels is low. Clear band heads, however, are missing. Moreover, the spin-

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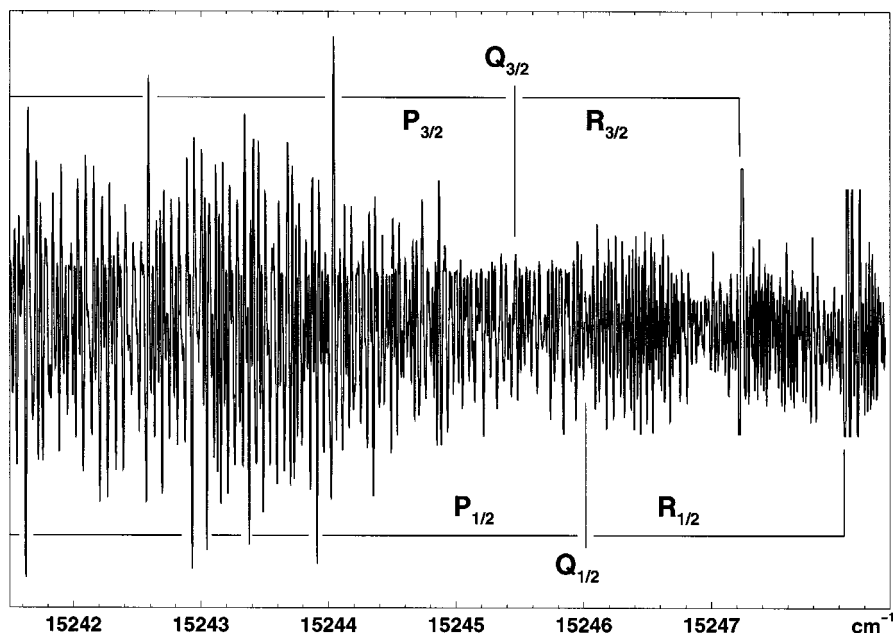


FIG. 1. Rotationally resolved frequency production double modulation absorption spectrum of the $A^2\Pi_u \leftarrow X^2\Pi_g$ electronic origin band of NC_6N^+ measured in a liquid-nitrogen cooled hollow cathode discharge ($T_{\text{rot}} \sim 150$ K). The P -, Q - and R -branches of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ and $A^2\Pi_{1/2} \leftarrow X^2\Pi_{1/2}$ subbands are indicated.

orbit components overlap as the difference in spin-orbit splittings in ground and excited state, ΔA , appears to be small. All these factors together lead to ambiguity in the assignment of the rotational lines. What is missing is a clearly defined starting point. This is provided by the jet spectrum.

In Fig. 2 part of the spectral region of Fig. 1 is shown. The spectrum is recorded by CRD in the plasma expansion. Only the lower subband, $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$, is clearly visible now, as the population of the upper spin-orbit component is low. Besides unresolved P - and R -branches,²² a clear Q -branch is observed starting at $15\,245.46(3)$ cm^{-1} . This branch is not visible in Fig. 1, but the CRD position allows the assignment of transitions belonging to the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ subband within ± 1 J quantum numbering in the FPM spectrum. The band gap is $\sim 10B$ [with $B \sim 0.019$ cm^{-1} (Ref. 18)] reflecting that the lowest rotational transitions cor-

respond to $P(\frac{5}{2})$ and $R(\frac{3}{2})$. Adjacent transitions are separated by $\sim 2B$. In this way more than 80(40) transitions have been assigned in $P(R)$ -branch of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ band with J -values up to 90.5.²³ These values are then fitted with PGopher²⁴ using ν_0 , B''_0 , B'_0 , D''_0 and D'_0 as variables yielding a rms of 0.002 cm^{-1} . The resulting constants are listed in Table I. The value for $B''_0 = 0.018\,753\,3(55)$ cm^{-1} is close to the B_e -value of $0.018\,67$ cm^{-1} as obtained from density functional calculations.¹⁸ A simulation using these constants proves that the stronger feature in Fig. 1 at $15\,247.23(3)$ cm^{-1} corresponds to the R -branch band head of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ system. A similar feature is observed at $15\,247.85$ cm^{-1} and is tentatively assigned to the R -branch band head of the second spin-orbit system.

The lines that are left over are mainly due to the $\Omega = \frac{1}{2}$

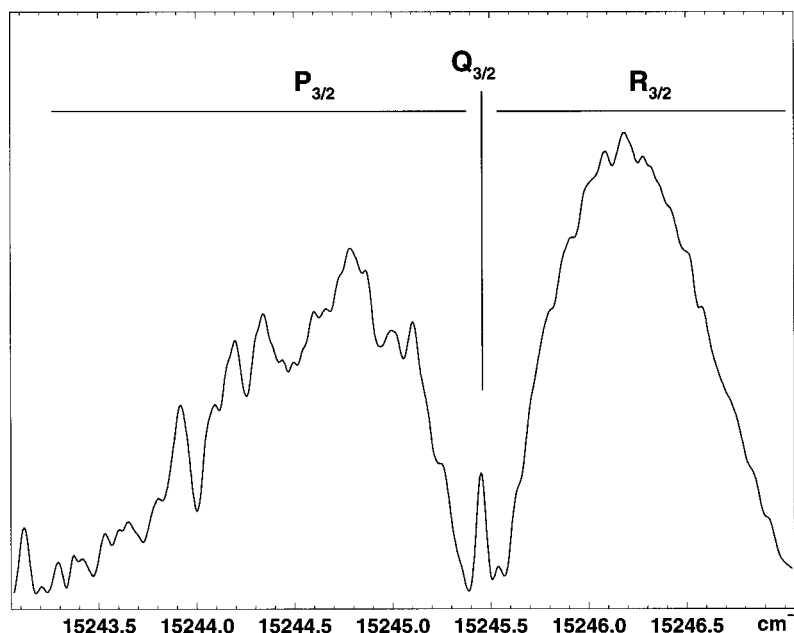


FIG. 2. Cavity ring down absorption spectrum of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ electronic origin band of NC_6N^+ , recorded through a supersonic plasma. The second spin-orbit component is not visible at the low temperature in the jet ($T_{\text{rot}} \sim 15$ K). The Q -branch position is used to assign the FPM spectrum.

TABLE I. Molecular constants (in cm^{-1}) for the $A^2\Pi_{3/2}-X^2\Pi_{3/2}$ and for the $A^2\Pi_{1/2}-X^2\Pi_{1/2}$ electronic origin band transition of NC_6N^+ . The molecular parameters for the $A^2\Pi_u-X^2\Pi_g$ electronic origin band transition of the iso-electronic HC_7N^+ (Ref. 17) and HC_8H^+ (Ref. 19) species are listed for comparison.

	NC_6N^+		HC_7N^+	HC_8H^+
	$\Omega=3/2$	$\Omega=1/2$	$\Omega=3/2$	$\Omega=3/2$ and $1/2$
B_0''	0.018 753 3(55)	0.018 707(19)	0.018 966 5(71)	0.019 077 9(93)
D_0''	6.7(15). 10^{-9}	6.2(38). 10^{-9}		
B_0'	0.018 558 5(56)	0.018 565(19)	0.018 773 1(72)	0.018 867 3(94)
D_0'	7.1(16). 10^{-9}	8.3(39). 10^{-9}		
ΔB	-0.00019	-0.00014	-0.00019	-0.00021
ΔA	+ 0.56		-2.04	-3.00
ν_0	15 245.737(1)		14 925.423(4)	14 143.1815(5)

component. The rotational assignment is problematic now as information on the Q -branch of the $A^2\Pi_{1/2}-X^2\Pi_{1/2}$ band is missing. The difference between the band heads, however, indicates that the $Q_{1/2}$ -branch is expected around 15246.1 cm^{-1} . In addition, only minor differences between the rotational constants for the two spin-orbit systems are expected. In previous studies transitions originating from different spin-orbit components were fitted with one single set of rotational parameters.^{7,16,19} In the present experiment this turns out not to be possible. However, as long as the effect of spin uncoupling is small, i.e., $2BJ \ll |A|$, B is best replaced by effective parameters $B_{\text{eff}}(^2\Pi_{1/2})$ and $B_{\text{eff}}(^2\Pi_{3/2})$. In second order perturbation theory the difference ΔB_{eff} is given by

$$\Delta B_{\text{eff}} = \frac{2B^2}{\bar{A}}, \quad (1)$$

where $\bar{A} = A - 2B$.²⁵ A is expected to be of the order of $-40(5) \text{ cm}^{-1}$ (Ref. 16) which puts an additional constraint to the fit. The line positions and most likely assignment for

transitions belonging to the $A^2\Pi_{1/2}-X^2\Pi_{1/2}$ system are available from (Ref. 26). The resulting molecular parameters are given in Table I. The quality of the fit will be worse as only a few transitions share a common level (rms $\sim 0.004 \text{ cm}^{-1}$).²⁶ Nevertheless, using Eq. (1) an A'' -value between -15 and -32 cm^{-1} is calculated.²⁷ The simulation confirms that the band head position coincides with the feature at 15247.85 cm^{-1} .

The spectral features of NC_6N^+ are expected to be qualitatively similar to those of the iso-electronic cyanotriacetylene cation¹⁷ and tetraacetylene cation.¹⁹ The molecular parameters of the $A^2\Pi_u-X^2\Pi_g$ electronic origin bands of these two ions are listed in Table I as well. These bands are shifted to lower energy, by 320 cm^{-1} for HC_7N^+ and by 1103 cm^{-1} for HC_8H^+ . The ΔA value of HC_7N^+ (-2.04 cm^{-1}) is comparable to that of HC_8H^+ (-3.00 cm^{-1}), but the corresponding value for NC_6N^+ is significantly smaller and, moreover, is positive ($+0.56 \text{ cm}^{-1}$). This value, however, is very close to the $\Delta A = +0.53 \text{ cm}^{-1}$ found for NC_4N^+ .¹⁶ There it was concluded that this anomaly is due to a spin-orbit induced interaction of the upper $A^2\Pi_{1/2}$ electronic state with another low lying electronic state, presumably of $^2\Sigma$ character, whereas the $A^2\Pi_{3/2}$ state is not affected. This becomes clear from the different values for $\Delta B = B_0' - B_0''$: for the $\Omega = \frac{3}{2}$ component a value of 0.00019 cm^{-1} is found, similar to the values determined for HC_7N^+ (0.00019 cm^{-1}) and HC_8H^+ (0.00021 cm^{-1}), but for $\Omega = \frac{1}{2}$ the value decreases to 0.00014 cm^{-1} . The second-order spin-orbit contribution to the rotational constant for a Π state is given by^{28,29}

$$B^{(2)} = \sum_{n \neq 0} \frac{4B^2}{E_0^0 - E_n^0}. \quad (2)$$

With $|\Delta E| = 40 \text{ cm}^{-1}$ this gives $B^{(2)} \sim 0.00004 \text{ cm}^{-1}$, i.e., an unperturbed value for ΔB of 0.00018 cm^{-1} , close to the value of the other spin-orbit component.

In the case of NC_4N^+ it was also found that the $^2\Sigma-^2\Pi$ interaction removes the degeneracy of the e - and

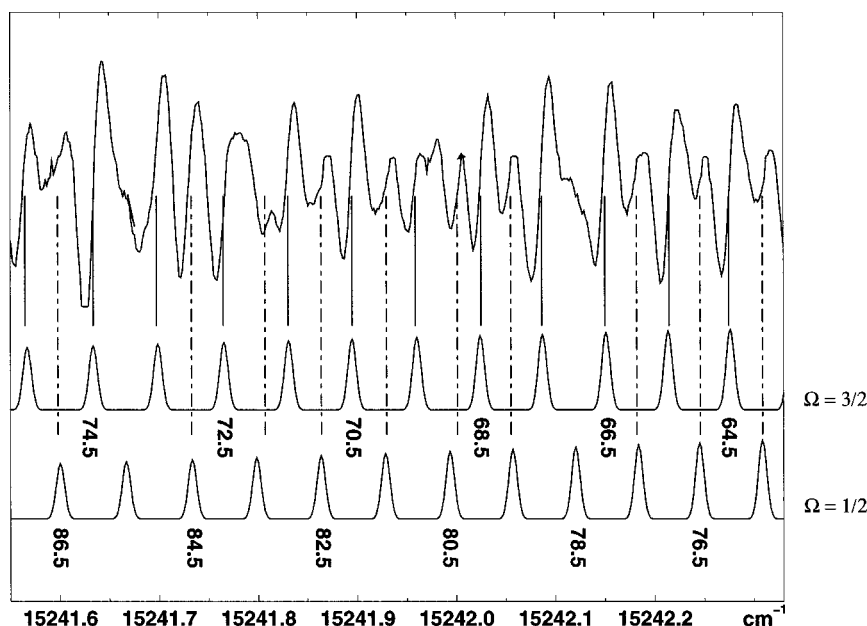


FIG. 3. High J -level transitions with their typical $1f$ derivative line shapes recorded in the FPM experiment. The simulated spectrum is shown for both spin-orbit components. There is no evidence for Λ -doubling (see the text).

f -symmetry, resulting in a resolvable Λ -doubling. This effect is not observed here. In Fig. 3 part of the P -branch range for high J -levels in both spin-orbit components is shown. The simulated spectrum is given as well. Clearly, there is no evidence for Λ -doubling within the experimental resolution: the size of the splitting would have been J -dependent and the expected 2:1 spin-statistical alternation is lacking. This is also expected: the rotational constant of NC_6N^+ is 2.5 times smaller than that of NC_4N^+ ($\sim 0.044 \text{ cm}^{-1}$) and since the Λ -type doubling constants p and q are proportional to B and B^2 , respectively, splittings will be considerably smaller.

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